



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  B01D 15/00, C02F 1/28	<b>A1</b>	<b>(11) International Publication Number:</b> WO 94/03249  <b>(43) International Publication Date:</b> 17 February 1994 (17.02.94)
<b>(21) International Application Number:</b> PCT/EP93/02029 <b>(22) International Filing Date:</b> 29 July 1993 (29.07.93)  <b>(30) Priority data:</b> 9201418                      7 August 1992 (07.08.92)                      NL  <b>(71) Applicant (for all designated States except US):</b> AKZO N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> BUIJTENHUIJS, Frederik, Albert [NL/NL]; Drentesingel 131, NL-6835 HM Arnhem (NL). PRAGT, Johanne, Josef [NL/NL]; Iepen- hof 14, NL-6951 MG Dieren (NL). SCHOMAKER, Elwin [NL/NL]; Tuinstraat 2, NL-68882 NX Velp (NL).		<b>(74) Agent:</b> SCHALKWIJK, P., C.; Akzo N.V., Patent Department (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).  <b>(81) Designated States:</b> AU, CA, CZ, FI, HU, JP, KR, NO, PL, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER  <b>(57) Abstract</b>  Use of a porous, preferably dimensionally stable, material for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, the material containing a hydrophobic substance exhibiting great affinity for the constituents to be extracted from the water, characterised in that the material has a surface which will be wetted more readily by the hydrophobic substance immobilised in the pores having an average diameter in the range of 0.1 to 50 µm than by the aqueous solution, with the proviso that at least 60 % of this substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

## MATERIAL FOR EXTRACTING HYDROPHOBIC COMPONENTS DISSOLVED IN WATER

5 The invention relates to the use of a porous, preferably dimensionally stable, material for the extraction of hydrophobic constituents, such as benzene, toluene, xylene and/or chlorinated hydrocarbons, from an aqueous solution, the material containing a hydrophobic substance exhibiting great affinity for the constituents to be extracted from the water.

10 Such a use, with a porous material being employed, was earlier described in GB-A-1 535 481. The porous material employed in this document consists of mineral carriers which are inert with respect to water, to the hydrophobic substance to be used as extractant, and to the compound to be extracted. Examples of suitable mineral carriers mentioned are pumice, kieselguhr, bauxite, alumina, carbon, or  
15 silicates. The particles preferably have a size in the range of 0,1 mm to 5 cm. It is stated that the pore size is critical only to the extent that it should be large enough to permit penetration of the compound to be extracted, of the extraction solvent, and of the regeneration liquid.

20 In actual practice, using the known materials for the aforementioned extraction process is attended with major drawbacks because the hydrophobic substances absorbed in them are easily displaced by water, especially when a packed bed is employed. In consequence, the water to be extracted or purified is in fact contaminated rather than  
25 decontaminated by these substances.

The invention now provides for the use of a porous material with a hydrophobic substance absorbed therein which, a significant increase  
30 in the capacity per volume unit notwithstanding, does not give rise to stability problems, not even when utilised on an industrial scale.

5 The invention consists in that when a porous material of the known type mentioned in the opening paragraph is used, it has a surface which will be wetted more readily by the hydrophobic substance immobilised in the pores of an average diameter in the range of 0,1 to 50  $\mu\text{m}$  than by the aqueous solution, with the proviso that at least 60% of the hydrophobic substance can be extracted from the pores by a liquid wholly made up of the constituents to be extracted.

10 To determine the average pore diameter advantageous use is made of mercury porosimetry in accordance with ASTM D 4248-83.

15 According to the invention, preference is given to the use of a porous material at least 85% of which can be extracted from the pores by a liquid wholly composed of the constituents to be extracted.

20 It is to be considered extremely surprising that by the use of a porous material having a hydrophobic surface as well as an average pore diameter within the given range both the stability and the extraction capacity are so enhanced that now, for the first time, application on an industrial scale has become feasible.

25 It was found that, in general, optimum results can be obtained when using a material having an average pore diameter in the range of 0,2 to 15  $\mu\text{m}$ .

30 The hydrophobic immobilised material may be solid matter as well as a liquid. If the immobilised material is a solid, preference is given to a polymer which swells in the hydrophobic substance to be extracted. Examples of polymers which are suitable for use within the framework of the invention include polymethyl(meth)acrylate, styrene-acrylonitrile copolymer, and acrylonitrile-butadiene-styrene copolymer, all of which may be partially cross-linked or not. Preference is given in this case to polystyrene. If the immobilised

material is a liquid, use is made of a liquid having the greatest possible affinity for the hydrophobic constituents to be extracted. Needless to say, this liquid should be virtually insoluble in the aqueous solution to be extracted and be so immobilised in the porous material that it cannot flow from the porous structure.

Within the framework of the invention preference is given to the use of a liquid in the form of a glycerol ester of one or more, preferably unsaturated, fatty acids.

In general, favourable results are attained if the immobilised liquid is an oil, such as palmitic oil, olive oil, peanut oil, paraffinic oil, fish oil such as herring oil, linseed oil, and, in particular, soybean oil and/or castor oil.

Generally, favourable results are attained when using a material of which at least 15 vol.% of the pores is filled with the substance immobilised therein, with optimum results being obtained using a material of which at least 50 vol.% and not more than 95 vol.% of the pores is filled with the substance immobilised therein. Completely-filled up pores may cause problems on account of swelling (solid matter) or expansion (liquid), which may lead to the dimensions of the porous material being interfered with or to the immobilised liquid bursting the pores. In the case of porous materials wholly filled up with a liquid hydrophobic substance being used, these difficulties can easily be overcome by mixing the filled material with unfilled (porous) material, so that the generated excess can be absorbed during extraction. Alternatively, when a packed bed is used, the unfilled (porous) material may be deposited at the two ends of the bed as separate boundary layers. When these types of steps are taken, 100 vol.-%-filled materials may also be employed.

The porous material preferably is organic in origin. However, it is also possible to use a porous inorganic material, providing it has a hydrophobic surface, e.g., through the application of a coating.

Within the framework of the invention preference is given to the use of natural and synthetic organic materials, the latter materials being preferred for reasons of reproducibility. Examples of synthetic organic materials include porous polymers, more particularly those of which the preparation is disclosed in US Patent Specification 4 247 498.

Examples of polymers deemed more or less suitable for use in the present invention include:  
low pressure polyethylene, high pressure polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene terpolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(4-methyl-pentene-1), and polybutene.

Optimum results were attained by employing polyolefin based polymers, with preference being given to the use of a polypropylene based porous material.

The porous polymer is generally used in the form of grains having an average particle diameter of 0,1 to 10 mm. Alternatively, the polymer may be employed in the granulated form, as well as in the form of membranes, fibres which may be hollow or not, etc.

When in the form of a granulate or a powder, the porous polymer may be used in a packed bed, a fluidised bed, or a tank with stirring. Fibres which may be hollow or not are used in the form of fabrics and non-wovens, respectively.

Particularly when a glycerol ester of one or more unsaturated fatty acids is employed to extract aromatic compounds from aqueous solutions, preference is given to a porous material obtained by a process such as described in DE-A-32 05 289. By this process a structure may be obtained which has pores of an average diameter in the range of 0,1 to 50  $\mu\text{m}$ . Especially favourable results may be

obtained when using polypropylene as porous material and soybean oil/castor oil as hydrophobic substance.

Needless to say, the materials according to the invention are not just suitable for extracting aromatic waste matter from aqueous solutions; extracting useful constituents such as biologically active constituents from usually highly dilute aqueous solutions is also within the bounds of possibility.

Generally, the procedure used to prepare the extracting material according to the invention is as follows: first, 5-90 wt.% of a polymer is dissolved, with heating, at a temperature above the upper critical decomposition temperature  $T_c$  in 10-95 wt.% of a mixture of two liquid and miscible compounds A and B, the mixing ratio of A to B being so selected as to give decomposition on cooling, resulting in a polymer-rich and a polymer-poor phase. On further lowering of the temperature this decomposition structure is then fixed prior to the completion of the phase separation, due to vitrification or crystallisation of the polymer, resulting in a porous polymer material filled with the mixture of compounds A and B which is pre-eminently suited to be used within the framework of the invention, either as such or after diminution if so desired.

The invention will be illustrated with reference to the following examples, which, of course, are not to be construed as limiting in any manner the scope of the invention.

## Example I

5 A glass column of 2 m in length and with a diameter of 23 cm, which at its top and bottom was closed up with perforated screens having apertures of 1 mm in diameter, was filled over a length of 180 cm with a porous polypropylene powder filled with oil (hydrophobic extractant).

10 Two experiments were carried out, the first one making use of polypropylene powder partially filled with soybean oil, the second one employing polypropylene powder wholly filled with soybean/castor oil. The two powders also differed from each other in terms of particle size distribution.

The powders in question had the following specifications:

	Powder I	Powder II
15 particle diameter	350 - 1000 $\mu\text{m}$	100 - 2000 $\mu\text{m}$
porosity	3 ml/g	3 ml/g
average pore diameter	10 $\mu\text{m}$	10 $\mu\text{m}$
degree of substitution	60 wt.%	72 wt.%
with oil		

20 In order to prevent the fine polypropylene powder from clogging up the apertures of the perforated screens, in each of the two arrangements the powder was bounded on either side by a 10 cm thick layer of the same material in the form of unfilled granules of 3-4 mm in diameter.

25 Powder I (7,38 kg) was filled with 11,06 kg of soybean oil to give a total of 18,44 kg.

Powder II (8,04 kg) was filled with 20,51 kg of soybean oil/castor oil to give a total of 28,55 kg.

30 The rate of flow of the liquid was 157 l per hour at a temperature of 24°C. The average overall aromatics content in the water to be purified was 840 ppm, the benzene content was 630 ppm, the toluene content 60 ppm.



In the case of powder I, the aromatics concentration in the effluent during an extraction process lasting well over 12 hours could not be measured. By then, the material had absorbed about 6,5 wt.% of benzene and 8,5 wt.% of aromatics, respectively.

5

In the case of powder II, the aromatics concentration in the effluent during an extraction process lasting well over 20 hours could not be measured. By then, the material had absorbed about 7 wt.% of benzene and 9 wt.% of aromatics, respectively. The point of saturation was reached after about 45 hours, when more than 15 wt.% of aromatics had been absorbed.

10

The aromatics content was measured intermittently by IR spectroscopy in accordance with ASTM D3921-85, the benzene content by liquid chromatography.

15

#### Example II

20

The column of Example I was now filled with 28,3 kg of powder II, which was bounded on either side by a 5-10 cm thick layer of unfilled polypropylene granules. The rate of flow of the liquid was 300 l per hour at a temperature in the range of 11° to 13°C. The water to be treated had the following influent concentrations:

chloroform                      0,5 ppm

25

carbon tetrachloride        32 ppm

30

After 4 hours in the loaded state, with the contaminated water flowing upwards from the bottom, the column was regenerated with 103°C steam for 4 hours, with the steam being passed through the column in opposite direction to the water. The rate of flow of the steam was 4 kg per hour. The subsequent periods of loading also were 4 hours each. After eleven of such loadings the efficiency of the column continued unchanged. The effluent concentrations of the treated water were measured by means of gas chromatography using an electron capture

detector (ECD) and found to be below the detection limit for chloroform and carbon tetrachloride of < 10 ppb (parts per billion), except that in the case of carbon tetrachloride values < 60 ppb were measured occasionally.

5 After condensation of the steam, the chloroform and carbon tetrachloride were drawn off from a liquid separator as lower layer.

### Example III

10 In a manner analogous to that disclosed in Example I, two glass columns of 2 m in length and 23 cm in diameter were installed. These columns likewise were closed up at the top and the bottom with perforated screens having apertures of 1 mm in diameter. In order to achieve better distribution over the columns of the powder to be introduced, the columns were filled with stainless steel Pall® rings  
15 of 15 mm in diameter before being filled over a length of 190 cm with porous powder completely filled up with soybean/castor oil. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 5-10 cm thick layer of identical material  
20 in the form of unfilled granules having a diameter of 3-4 mm.

The specification of the powder was as follows:

particle diameter	350-1000 $\mu\text{m}$
porosity	3 ml/g
average pore diameter	10 $\mu\text{m}$
25 degree of substitution	
with oil	72 wt.%

The amounts of powder differed per column: column 1 held 24,4 kg and column 2 29,4 kg.

30 The columns were loaded alternately, with the water to be treated being pumped from the bottom upwards and regeneration with 105°C atmospheric steam taking place from the top downwards. The rate of flow of the steam was 4 kg per hour.

After 32 loadings and regenerations the efficiency of the columns

proved unchanged.

The rate of flow of the liquid was 150 l per hour at a temperature of 6° to 13°C. The water to be treated had the following influent concentrations:

5	dichloromethane	195 ppm
	chloroform	39 ppm
	dichloroethane	32 ppm
	benzene	272 ppm
	toluene	137 ppm

10 The effluent concentrations were measured by means of gas chromatography using an electron capture detector (for chlorinated hydrocarbons) and flame ionisation (for benzene and toluene), respectively, and found to be below the detection limits for  
15 chloroform, dichloroethane, benzene, and toluene of 10 ppb (for chloroform and dichloroethane) and 1 ppb (for benzene and toluene), respectively. The value measured for dichloromethane each time was < 0,6 ppm.

20 Example IV

In a manner analogous to that disclosed in Example III, two columns were filled with Pall® rings, which this time had a diameter of 25 mm and were made of polypropylene. The columns were filled over a length  
25 of 180-190 cm, column 1 being filled with 28,3 kg of powder and column 2 with 23,8 kg. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 5-10 cm thick layer of unfilled polypropylene granules having a diameter of 3-4 mm. The regeneration was carried out at a rate of flow of the steam of  
30 2 kg per hour. After 11 loadings and regenerations the efficiency of the columns proved unchanged.

The rate of flow of the liquid was 150 l per hour at a temperature of 15° to 20°C. The water to be treated had the following influent

concentrations:

	1,1-dichloroethane	2-3	ppm
	cis-1,2-dichloroethene	30-50	ppm
	1,1,1-trichloroethane	1-8	ppm
5	trichloroethene	0,1-0,3	ppm

Again, the effluent concentrations were measured by means of gas chromatography using ECD and found to be below the detection limits for said solvents, which were as follows:

10	1,1-dichloroethane	< 50	ppb
	cis-1,2-dichloroethene	< 150	ppb
	1,1,1-trichloroethane	< 1	ppb
	trichloroethene	< 1	ppb

15 After condensation of the steam the organic substances were drawn off from a liquid separator as lower layer.

#### Example V

20 In a manner analogous to that disclosed in Example IV, two columns were filled with Pall® polypropylene rings of 25 mm in diameter. Next, the columns were filled, over a length of 170 cm, with porous unfilled polypropylene powder. In order to prevent clogging up of the perforated screens, the powder was bounded on either side by a 10-20  
25 cm thick layer of unfilled polypropylene granules having a diameter of 3-4 mm.

The specification of the powder was as follows:

	particle diameter	350-1000 $\mu$ m
	porosity	3 ml/g
	average pore diameter	10 $\mu$ m
30	degree of substitution	
	with oil	0 wt.%

Column 1 contained 7,22 kg of unfilled powder, column 2 held 7,26 kg.

First, xylene was passed through the columns until the pores were wholly filled with xylene and there was xylene sticking to the powder particles.

Next, there was alternate loading of the columns, with the water to be treated again being pumped through the column from the bottom upwards. The regenerant used was xylene of 20° to 50°C, which was passed through the column from the top downwards. The rate of flow of the xylene was 55 l per hour. After being regenerated, the columns were emptied with nitrogen, with the powder retaining 30 kg of xylene as extractant.

The rate of flow of the waste water to be treated was 150 l per hour at a temperature of 20° to 50°C.

The water to be treated had the following influent concentrations:

	o-cresol	70 - 250 ppm
15	2-methyl-4-chlorophenoxyacetic acid	50 - 160 ppm
	2,4-dichlorophenoxyacetic acid	1 - 20 ppm
	6-chloro-o-cresol	50 - 200 ppm
	4-chloro-o-cresol	90 - 200 ppm
	2-(2,4-dichlorophenoxy)propionic acid	4 - 7 ppm
20	2-(2-methyl-4-chlorophenoxy)propionic acid	3 - 13 ppm
	4,6-dichloro-o-cresol	7 - 16 ppm

Measurement of the effluent concentrations this time was by means of liquid chromatography using UV detection. The two columns had the same effluent compositions, with the measured concentrations always being lower than the following values:

	o-cresol	< 1 ppm
	2-methyl-4-chlorophenoxyacetic acid	< 1 ppm
	2,4-dichlorophenoxyacetic acid	<0,4 ppm
30	6-chloro-o-cresol	<0,5 ppm
	4-chloro-o-cresol	<0,5 ppm
	2-(2,4-dichlorophenoxy)propionic acid	<0,2 ppm
	2-(2-methyl-4-chlorophenoxy)propionic acid	<0,2 ppm
	4,6-dichloro-o-cresol	<0,1 ppm

CLAIMS

- 5      1.      Use of a porous, preferably dimensionally stable, material for  
the extraction of hydrophobic constituents, such as benzene,  
toluene, xylene and/or chlorinated hydrocarbons, from an  
aqueous solution, the material containing a hydrophobic  
substance exhibiting great affinity for the constituents to be  
10      extracted from the water, characterised in that the material  
has a surface which will be wetted more readily by the  
hydrophobic substance immobilised in the pores having an  
average diameter in the range of 0,1 to 50  $\mu\text{m}$  than by the  
aqueous solution, with the proviso that at least 60% of this  
15      substance can be extracted from the pores by a liquid wholly  
made up of the constituents to be extracted.
2.      Use according to claim 1, characterised in that the average  
pore diameter is in the range of 0,2 to 15  $\mu\text{m}$ .
- 20      3.      Use according to claim 1, characterised in that at least 85% of  
the immobilised hydrophobic substance can be extracted from the  
pores by a liquid wholly made up of the constituents to be  
extracted.
- 25      4.      Use according to claim 1, characterised in that at least 15  
vol.% of the pores is filled with the substance immobilised  
therein.
- 30      5.      Use according to one or more of the preceding claims,  
characterised in that the immobilised substance is a polymer  
which swells in the hydrophobic substance to be extracted.

6. Use according to one or more of claims 1-4, characterised in that the immobilised substance is polystyrene.
- 5 7. Use according to claim 1, characterised in that the immobilised substance is a liquid.
8. Use according to claim 1, characterised in that the immobilised substance is a glycerol ester of one or more, preferably unsaturated, fatty acids.
- 10 9. Use according to claim 8, characterised in that the immobilised glycerol ester is soybean oil and/or castor oil.
- 15 10. Use according to claim 1, characterised in that the porous material is a polyolefin.
11. Use according to claim 10, characterised in that the porous material is polypropylene.
- 20 12. Use according to claim 1, characterised in that the porous material is obtained by the dissolving of a polymer in a solvent with heating, the cooling of the solution, and the mechanical diminution of the solidified mass if so desired.
- 25 13. Use according to claim 12, characterised in that the polymer is polypropylene and the solvent is soybean oil and/or castor oil.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B01D15/00 C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NL,A,7 701 328 (IFP) 15 August 1977 cited in the application see page 2, line 1 - page 6, line 2	1,4,6
A	US,A,4 276 179 (SOEHNGEN) 30 June 1981 see column 2, line 45 - column 5, line 2 see column 13, line 63 - column 15, line 25	1,2,7-11
A	FR,A,2 251 525 (COMP. FR. DE RAFFINAGE) 13 June 1975 see page 12-13; claims 1-16	1,7,10, 11
A	DE,A,36 32 360 (BÜSLING) 31 March 1988 see column 1; claims 1-9 see column 3, line 49 - column 4, line 7	1,5,6
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 October 1993

Date of mailing of the international search report

05.11.93

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

WENDLING, J



C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 115 425 (AKZO) 7 September 1983 cited in the application see page 9-10; claims 1-23 ---	12
A	EP,A,0 106 970 (AM. CYANAMID CO.) 2 May 1984 ----	
A	EP,A,0 248 429 (PASSAVANT-WERKE) 9 December 1987 -----	

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
NL-A-7701328	15-08-77	FR-A- 2340910	09-09-77
		BE-A- 851080	04-08-77
		DE-A- 2704569	18-08-77
		GB-A- 1535481	13-12-78
		JP-A- 52098676	18-08-77
US-A-4276179	30-06-81	CA-A- 1135680	16-11-82
FR-A-2251525	13-06-75	NONE	
DE-A-3632360	31-03-88	NONE	
GB-A-2115425	07-09-83	DE-A- 3205289	25-08-83
		CA-A- 1231210	12-01-88
		FR-A, B 2521572	19-08-83
		JP-A- 58164622	29-09-83
		SE-B- 449368	27-04-87
		SE-A- 8300766	16-08-83
		US-A- 4594207	10-06-86
EP-A-0106970	02-05-84	US-A- 4470909	11-09-84
		AU-A- 1976883	05-04-84
		CA-A- 1219881	31-03-87
		JP-A- 59082989	14-05-84
		CA-A- 1196621	12-11-85
EP-A-0248429	09-12-87	DE-A- 3618698	10-12-87
		DE-A- 3784968	29-04-93
		EP-A- 0457359	21-11-91
		US-A- 4842745	27-06-89